

## IMPROVEMENT OF CO<sub>2</sub> PURIFYING SYSTEM BY PHOTOCATALYST FOR APPLICATION IN MICROALGAE CULTURE TECHNOLOGY

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### ABSTRACT

By reactive grinding method Vanadium-doped rutile TiO<sub>2</sub> nanoparticle material was obtained with an average particle size of 20-40nm, the Brunauer–Emmet–Teller (BET) specific surface area about 20 m<sup>2</sup>g<sup>-1</sup> and it absorbed strongly in the UV region and increased at the visible wavelength of 430 – 570 nm. This study focused on the improvement of exhaust gas treatment from coal-fired flue gas of the traditional adsorption-catalysis system (Modular System for Treating Flue Gas - MSTFG) by using the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> Rutile as photocatalyst. The results showed that integrating both catalytic systems mentioned above increased the gas treatment efficiency: CO from 77 % to over 98 %, NO<sub>x</sub> from 50 % to 93 %, SO<sub>2</sub> was absent as opposed to the input gas component. Also it showed that V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> Rutile integrated with MSTFG has got high efficiency of CO treatment, also secured the high obtained CO<sub>2</sub> concentration as a valuable carbon source for microalgal mass culture as well as saving energy and simplifying devices.

**Keywords:** traditional adsorption-catalysis system, photocatalyst, integrating, coal-fired flue gas, carbon source.

### 1. INTRODUCTION

Process of burning coal can emit kinds of exhaust harmful gas out to atmosphere such as dust particles with minor sizes (PM), SO<sub>x</sub>, NO<sub>2</sub>, VOCs and a big volume of CO<sub>2</sub> gas, which participate in increase of the greenhouse effect, resulting in increase of the earth temperature leading to global climate change [1, 2].

Volume of CO<sub>2</sub> emitted in the exhaust gases was salvaged as material for different technological processes, which have been applied in many countries in the world. Eliminating

accompanied exhaust gas and isolation of CO<sub>2</sub> as a Carbon source for algae culture also included in the strategy mentioned above and is one of the advanced technologies in the going green of the century [3]. In Vietnam, we started using catalysts/absorbents able to convert harmful exhaust gases (NO<sub>x</sub>, CO, C<sub>x</sub>H<sub>y</sub>, VOCs) into H<sub>2</sub>O, N<sub>2</sub>, CO<sub>2</sub> in order to improve cleanness of CO<sub>2</sub> used in *Spirulina* culture [3]. However, the catalytic system with the length of 60 cm and section of 25×25 cm<sup>2</sup> used in our previous study [3] showed that the exhaust gases generated from burning coal have been treated with no high efficiency: only more than 70 % CO, 90 % SO<sub>x</sub> and 50 % NO<sub>x</sub> at temperature of 310 – 320 °C. So, for reaching higher efficiency it is required to extend the catalytic system as with the length twofold. On the other hand, temperature for converting the harmful gases on catalyst at 320 °C consumes rather big amount of energy for operation. To overcome the two mentioned above drawbacks, we recommend the use of photocatalytic system connected in series with the current treatment system.

Photocatalyst can work in normal temperature under sun light. Thus, photocatalytic material is promising component in technology for air purifying [4], decreasing series of pollutants in water environment [5]. In the world, there were many publications on photocatalytic material having high ability of application [4, 5, 6, 7]. Results obtained in the study [5] showed that TiO<sub>2</sub> materials of Rutile type denatured by Vanadium able to work in visible light area with rather high efficiency: fabricated TiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> not only well absorbs light in the ultraviolet light area but also rather highly absorbs the light with wave length of 400 – 600 nm; This material is also good catalyst for degrading methylene blue at normal light and room temperature. In this work, we fabricated TiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> photocatalyst, tested for CO conversion reaction in order to replace the traditional catalytic system described in paper [3].

## **2. SUBJECT AND METHODOLOGY**

### **2.1. Studied subject**

Exhaust gases including CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, CO,...in which CO<sub>2</sub> generated from burning coal are removed from accompanied exhaust gases by catalytic – absorption technology.

V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> Rutile photocatalytic material.

### **2.2. Methodology and equipment**

Exhaust gases were determined by equipment of MX6 and CA-6203, Testo 350-XL Emission Analyzer. Treating accompanied exhaust gases and cleaning CO<sub>2</sub> by traditional exhaust gas treatment modular system (EGTMS) were integrated with V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> photocatalytic material system.

Rutile TiO<sub>2</sub> was used as initial material with particle size bigger than 100 nm. Nano vanadi – doped rutile TiO<sub>2</sub> material was obtained by the reactive grinding method [5]. UV-Vis Absorption spectra of TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> samples were measured by CARRY 5000 UV-Vis-NIR equipment. Specific surface area of Brunauer-Emmett-Teller (BET) of samples was determined by nitrogen physical absorption method at 77 K. Size of particles was determined Scanning Electron Microscope (SEM). Concentration of CO was determined by Landcom II machine, U.K.

### 3. RESULTS AND DISCUSSION

#### 3.1. Photocatalytic material fabrication

According to the paper [5] we carried out fabrication of  $\text{TiO}_2$  mixed with vanadium by reactive grinding method via high-energy. The optimal time for grinding samples to synthesize  $\text{V}_2\text{O}_5/\text{TiO}_2$  was selected to be 4 hours.  $\text{TiO}_2$  rutile and  $\text{V}_2\text{O}_5$  in ratio 95:5 were dried at  $120^\circ\text{C}/2$  hours then was grinded by high energy mill (Spex 8000 M). This machine used two balls, including one with  $\Phi 15$  mm and the other with  $\Phi 5$  mm made of WCx hard steel. Mixture of 9.5g  $\text{TiO}_2$  and 0.5g  $\text{V}_2\text{O}_5$  was put into a hard steel container with inner volume of  $50\text{ cm}^3$ . The obtained material after 4 milling hours was examined in structure, size (by XRD method), morphology (by SEM photo), BET surface properties, light absorption capacity (by electronic absorption spectrometry) and accessed the activity on CO into  $\text{CO}_2$  conversion reaction.

#### 3.2. Determination of material structure by X-ray diffraction diagram X (XRD)

Figure 1 is X-ray diffraction diagram X of initial  $\text{TiO}_2$  and vanadium mixture material after grinding. It can be seen from the diagram, typical peaks of  $\text{TiO}_2$  appeared in form of rutile but peaks of  $\text{V}_2\text{O}_5$  are absent (for ground material). Typical pics of initial  $\text{TiO}_2$  samples were higher and narrower than that of  $\text{V}_2\text{O}_5/\text{TiO}_2$  ground after 4 hours. Thus, it can be seen that ground  $\text{V}_2\text{O}_5/\text{TiO}_2$  particles had significantly smaller sizes compared to initial  $\text{TiO}_2$  material.

On X-ray diffraction diagram of  $\text{V}_2\text{O}_5/\text{TiO}_2$  samples, there were not typical peaks of Vanadium Oxide appearing. Non appearance of typical Vanadium Oxide could be due to the fact that Vanadium Oxide content was below the detectable threshold of the method or Vanadium Oxide's even desperation in the system or vanadium's existence in other forms in the crystal system of titanium oxide. This result was similar to [5]. Accordingly, in spite of non appearance of Vanadium Oxide peaks on X-ray diffraction diagram, the XAS analysis result (X-ray absorption spectrometry) indicated the existence of state of  $\text{V}^{4+}$  replacing  $\text{V}^{5+}$ , that means vanadium displacing  $\text{Ti}^{4+}$  or lying at empty position of  $\text{TiO}_2$  structure. So it can be said that a part of vanadium existed in form of  $\text{V}_2\text{O}_5$  evenly dispersed and a part existed in form of  $\text{V}^{4+}$  lying in  $\text{TiO}_2$  crystal network.

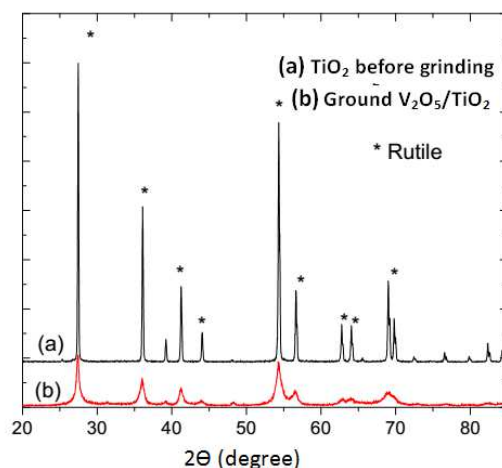


Figure 1. XRD patterns of Rutile  $\text{TiO}_2$  before grinding (a) and ground  $\text{V}_2\text{O}_5/\text{TiO}_2$  for 4 hours(b).

### 3.3. Determining morphology, particle size and the BET specific surface area

Figure 2 is SEM image of the material. We can see that TiO<sub>2</sub> before grinding (a) had size of 100 – 130 nm, after grinding and mixed with vanadium (b) had size of 20 - 40 nm. After determining specific surface area (BET) and comparing the typical features with the sample fabricated in paper [5] represented in table 1, it is seen that the previously fabricated samples and the present one are rather similar. This also confirms the material fabrication process was stable.

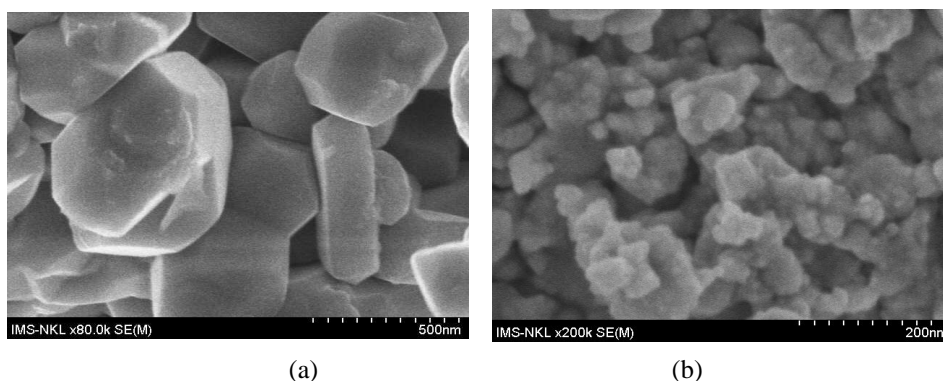


Figure 2. Scanning electron microscopy image (SEM) of Rutile TiO<sub>2</sub> before grinding (a) and (b) ground V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> for 4 hours.

Table 1. Particle size and the BET specific surface area of materials.

Samples	Grinding time (h)	Average particle size (nm)	BET (m <sup>2</sup> /g)
TiO <sub>2</sub>	0	100-130	1,19
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	4	20-40	19,5
[5] V <sub>2</sub> O <sub>5</sub> / TiO <sub>2</sub>	4	22	20,80

### 3.4. UV-Vis absorption spectrum of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> photocatalyst materials

Figure 3 is the light absorption spectrometry of unground TiO<sub>2</sub> rutile (a) and ground V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> after 4 hours (b). We can see that the unground TiO<sub>2</sub> sample absorbed light at wave length less than 420 nm, while the mixed and milled sample after 4 hours absorbed light at longer-wave length in 430 - 570 nm area. This result can be compared with some anatase TiO<sub>2</sub> and TiO<sub>2</sub> Rutile previously published of authors Anpo et. al [6] and Liu et. al [7]. Thus, obtained material had rather big nano size and specific surface area, at the same time was denatured by vanadium (be considered as the most brilliant value in the series of metals used as doping for TiO<sub>2</sub>) promising a high activity of photo catalyst.

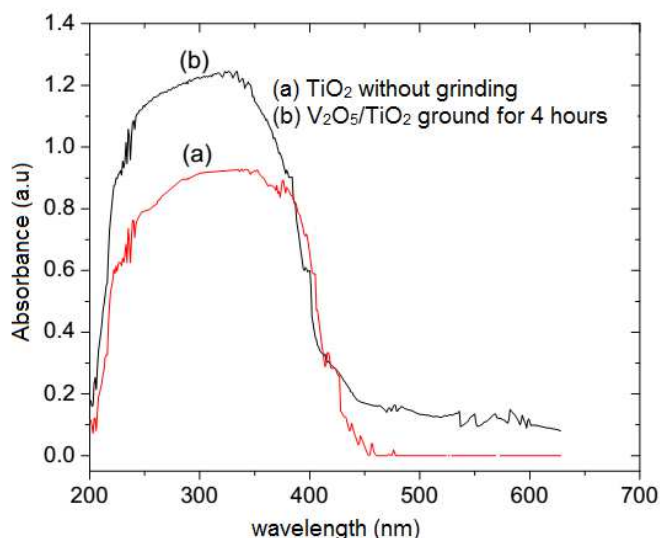


Figure 3. UV-Vis absorption spectra of Rutile  $\text{TiO}_2$  before grinding (a) and (b) ground  $\text{V}_2\text{O}_5/\text{TiO}_2$  for 4 hours.

### 3.5. The test on application of $\text{V}_2\text{O}_5/\text{TiO}_2$ Rutile photocatalytic material in treating exhaust gas generated from burning coal in semi-pilot scale

We carried out the test on treating exhaust gas generated from burning coal in two stages (Figure 4): 1. Initial exhaust gas was treated for the first time via a traditional catalytic system (A) – exhaust gas treatment modular system – with dimensions of  $60 \times 25 \times 25 \text{ cm}^3$ , operating at temperature  $320^\circ\text{C}$ . Exhaust gas after being treated by the traditional catalytic system has rather high temperature will be cooled to the room temperature system (B). 2. The volume of cooled gas was treated for the second time by photocatalytic material designed by 3 rock crystal modules, each had diameter of 0.7cm containing 1g photocatalytic material (C). The exhaust gas after the two said treatment stages was collected into gas collector (D). Concentration of gas components after each stage was determined and served for calculating the treatment efficiency of each stage.

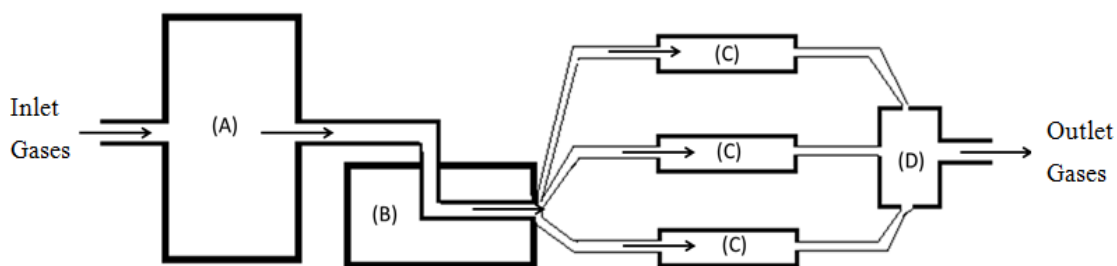


Figure 4. Diagram of the flue gas treatment from coal combustion. A: The traditional Modular system of Exhausted Gas Treatment; B: The gas cooling system at room temperature; C: Quartz tube; D: The purified gas storing system.

Table 2. Components of coal-fired flue gases inlet and outlet analysis

Components	Inlet of gases	The period after treating via traditional MEGT systems		The period after treating via photocatalyst systems	
		Concentration	Efficiency of reduction (%)	Concentration	Efficiency of reduction (%)
CO (ppm)	2000	454	77,3	38	98,1
SO <sub>2</sub> (ppm)	16 – 22	2	> 87,5	0	100
NO <sub>x</sub> (ppm)	30 – 32	16	> 46,7	2	93
CO <sub>2</sub> (%)	4,64	6,03	-	6,47	-

Obtained results in table 2 showed that the exhaust gas generated from burning coal after going through Exhaust Gas Treatment Modular System with traditional catalyst integrated with V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> photocatalytic material system was very well treated: the converted CO was more than 98 %, SO<sub>2</sub> – 100 % and NO<sub>x</sub> – 93 %, respectively compared to the composition of the input exhaust gas. Volume of CO<sub>2</sub> obtained was rather high, from 4.54 % increased to more than 6.47 % quite good for microalgae culturing.

#### 4. CONCLUSION

V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> photocatalytic material system was successfully fabricated with size 20 – 40 nm, BET specific surface area is of approximately 20 m<sup>2</sup>/g. This material strongly absorbs light in both UV area and 430 – 570 nm wave length area.

V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> photocatalytic material was a good catalyst for CO, NO<sub>x</sub> and SO<sub>2</sub> conversion process. The integration of a traditional catalytic system (A) – Exhaust Gas Treatment Modular System with V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> photocatalytic material system increased treatment efficiency of exhaust gases: CO from 77 % up to 98 %, NO<sub>x</sub> from 50% up to 93 % and 100 % for SO<sub>2</sub> compared to the input exhaust gas composition. The rather high CO<sub>2</sub> concentration- 6.47 %, is quite good carbon source for microalgae cultivation.

In the economical point of view, The EGTMS with traditional catalysts operating at comparatively high temperature 320 °C (Project KC08.08/11-15) intergrated with V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> photocatalytic material system operating at the room temperature will help to significantly reduce equipment size.

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### TÓM TẮT

#### CẢI THIẾN HỆ THỐNG LÀM SẠCH CO<sub>2</sub> BẰNG XÚC TÁC QUANG NHẪM ỨNG DỤNG TRONG CÔNG NGHỆ NUÔI TẢO

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Bằng phương pháp nghiền phản ứng, vật liệu xúc tác quang Nano Vanadi – doped Rutile TiO<sub>2</sub> chế tạo được có kích thước 20 – 40 nm, diện tích bề mặt riêng BET gần 20 m<sup>2</sup>/g, vật liệu hấp phụ mạnh trong vùng UV đồng thời tăng sang vùng bước sóng dài 430 – 570 nm. Bài báo này nghiên cứu khả năng cải thiện hiệu quả xử lý khí thải của Hệ Modul xử lý khí thải (HMĐXLKT) xúc tác truyền thống bằng việc kết nối thêm hệ modul sử dụng xúc tác quang V<sub>2</sub>O<sub>5</sub>/ TiO<sub>2</sub>. Kết quả cho thấy việc tích hợp hai hệ xúc tác nói trên đã làm tăng hiệu quả xử lý khí CO từ 77 % lên trên 98 %, NO<sub>x</sub> từ 50 % lên 93 % và làm sạch hoàn toàn SO<sub>2</sub> so với thành phần khí đầu vào. Điều này cho thấy hiệu quả của việc sử dụng hệ vật liệu xúc tác quang V<sub>2</sub>O<sub>5</sub>/ TiO<sub>2</sub> trong quá trình xử lý triệt để CO, đồng thời vẫn đảm bảo hàm lượng CO<sub>2</sub> thu được khá cao đáp ứng cho quá trình nuôi tảo như một nguồn cacbon giá trị, tiết kiệm được năng lượng và vận hành đơn giản.

*Từ khóa:* hệ thống xúc tác/ hấp phụ truyền thống, xúc tác quang, tích hợp, khí thải đốt than, nguồn cacbon.